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The Effect of Substitution on the Ionization Potentials of

Free Radicals and Molecules. V Extension of the Density

Matrix Treatment to a Two-Body Model for Electrons

Outside a "Core".

by

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Abstract

Extension has been made to a two-body model for a pair of electrons outside a "core" of the treatment by density matrix formulism of a one-body model for an electron outiside a "core". δ_k values [differences in ionization potentials between the parent compound] for the π electron of alkyl radicals can be developed exactly as a one-body model problem in terms of density matrices. The derivation of the two-body model permits one quantum mechanically to describe the same δ_k effects on the ionization potentials of an electron from the lone pair of substituted amines by an analogous treatment using the same perturbation Hamiltonian as for substituted alkyl radicals with two electron functions for the lone pair of the nitrogen.

Introduction

In part II of the series[1] the constancy of δ_k values [which measure the change in ionization potential between a substituted molecule (or radical) and the parent compound] for alkyl radicals and amines was discussed in relation to the energies and possible wave functions for these species and their positive ions in terms of ordinary first order perturbation theory. In that article it was assumed that at least in the alkyl radicals one could separate the σ and π electrons and, to a first approximation, deal with the Hamiltonian, wave function, and orbital of only the π electron. The basis for the above assumption at that time was that this separation is the one commonly invoked in virtually all theoretical treatments of π systems. However, verification for the separation in the case of alkyl radicals can now be based on the recent justification of the one-body model for an electron outside a "core"[2] which was derived in terms of density matrices. The problem of the alkyl radicals can also be developed exactly as a one-body model in terms of density matrix formulism.

In II it was shown to be possible to describe the wave functions and Hamiltonians for the substituted and unsubstituted amines in a manner which emphasizes their close similarity to the alkyl radicals by making a formal separation into σ and "π-like" electrons, where "π-like" implied only that this system is orthogonal to the other bonds in the molecule. This division depended upon the proven fact that it is possible to write the wave function for the

complete molecule as a product of wave functions which must be mutually orthogonal for the separate bonds or lone pairs so that certain orbitals may be associated with selected parts.[3] Later in this article it will be seen that the one-body model suitable for describing the alkyl radicals can be extended to a two-body model for a pair of electrons outside a "core" suitable for describing the amines.

Extension to Two-Body Model

The pertinent parts of the article on the one-body model[2] are summarized here to make it easier to follow its extension to the two-body model and its subsequent application to the alkyl radicals and amines.

Resume of One-Body Model

The system comprising a core and one valence electron was described by a wave function

$$\Psi(1,2,\ldots N) = M \, \mathcal{A}\{\Phi_A(1,2,\ldots[N-1]) \, \Phi_B(N)\} \tag{1}$$

where $\Phi_A(1,2,\ldots[N-1])$ is an antisymmetrical core function, $\Phi_B(N)$ is the spin orbital of the valence electron, $\mathcal{A}$ is the antisymmetrizer and M is the normalization factor. For convenience Φ_A and Φ_B were individually assumed to be normalized. No other assumptions were made and although (1) cannot be an exact wave function it provides a rather general description of a system with two distinguishable parts. The variational solution of

$$h_{eff} \, \Psi = \epsilon \, f \, \psi \tag{2}$$

proceeded even without orthogonality restrictions.

The density matrices of the whole system can be expressed in terms of those of its separate parts.

Definition of density matrix:

$$\rho_n \ (1,2,\ldots n;1',2',\ldots n') =$$

$$=\frac{N!}{(N-1)!} \int \Psi(1,\ldots N) \ \Psi^*(1',\ldots n';\overline{n+1},\ldots N)dx_{n+1}\ldots dx_N \qquad (3)$$

With analogous group density matrices ρ_n^A and ρ_n^B one obtained

$$\rho_1(1;1') = \{\rho_1^A(1;1') + \rho_1^B(1;1')\} - \underline{\quad\quad} \qquad (4)$$

$$\rho_2(1,2;1',2') = \{\rho_2^A(1,2;1',2') + \rho_1^A(1;1') \ \rho_1^B(2;2') \qquad (5)$$

$$- \rho_1^A(2;1') \ \rho_1^B(1;2') + \rho_1^B(1;1') \ \rho_1^A(2;2')$$

$$- \rho_1^B(2;1') \ \rho_1^A(1;2')\} - \underline{\quad\quad}$$

neglecting normalization constants and keeping only terms which remain when the functions Φ_A and Φ_B are orthogonal in the strong sense:

$$\int \Phi_A(1,i,j--) \ \Phi_B(1)dx_1 = 0 \qquad (6)$$

The remaining terms would arise from penetration of the valence electron into the core.

The energy of the whole system is given by

$$E = tr \ h(1) \ \rho_1(1;1') + \tfrac{1}{2}tr \ g \ (1,2) \ \rho_2(1,2;1',2') \qquad (7)$$

where h(1) is a modified one-body operator which depends on the core wave function, $g(1,2) = \dfrac{e^2}{r^{12}}$ and tr indicates removal of primes (after operation) and integration over all remaining variables.

It was then shown that

$$E = E^A + E^B_{eff} = E^A + \widetilde{E}^B \tag{8}$$

where E^A is the energy of the core by itself

$$E^A = tr\ h(1)\ \rho^A_1(1;1') + \tfrac{1}{2}tr\ g(1,2)\ \rho^A_2(1,2;1',2') \tag{9}$$

and $\widetilde{E}^B$ is the energy of the valence electron itself in an effective field due to the core.

$$\widetilde{E}_B = tr\ h(1)\ \rho^B_1(1;1') + tr \int g(1,2)\ \rho^A_1(2;2)dx_2\ \rho^B_1(1;1')$$

$$- tr \int g(1,2)\ \rho^A_1(1;2)\ \rho^B_1(2;1')dx_2 \tag{10}$$

$\widetilde{E}^B$ was expressed as

$$\widetilde{E}_B = tr\ \widetilde{h}^B(1)\ \rho^B_1(1,1') \tag{11}$$

where $\widetilde{h}^B(1)$ is an integral operator defined by

$$\widetilde{h}^B(1)\ \phi(1) = \int \widetilde{h}^B(1;2)\ \phi(2)dx_2 \tag{12}$$

$\widetilde{h}^B(1;2)$ - the kernel - consists of several terms and the operator is a corresponding sum of operators

$$\widetilde{h}^B(1) = h(1) + \,^A(1) - \mathcal{K}^A(1) + penetration\ terms \tag{13}$$

$$\,^A(1) \rightarrow J^A(1) = \int g(1,2)\ \rho^A_1(2;2)dx_2 \tag{14}$$

$$\mathcal{J}^A(1) \to K^A(1;2) = g(1,2) \, \rho_1^A(1;2) \tag{15}$$

$\mathcal{J}^A(1)$ and $\mathcal{K}^A(1)$ are the Coulomb and exchange potentials due to the core which are present even when (6) is satisfied.

Two-Body Model

For the two-body model for a pair of electrons outside a "core" keeping only the terms which remain when Φ_A and Φ_B are orthogonal according to (6), one now gets an additional term in the second order density matrix (5)

$$+ \rho_2^B(1,2;1',2') \tag{16}$$

When the expressions for the first and second order density matrices are substituted into the formula for the energy the following expression is obtained for the integral operator $\tilde{h}^B(1)$

$$\tilde{h}^B(1) = h(1) + \mathcal{J}^A(1) - \mathcal{K}^A(1) + \tfrac{1}{2}\mathcal{J}^B(1) - \tfrac{1}{2}\mathcal{K}^B(1) \tag{17}$$

where it must now be remembered that there is a pair of electrons in Φ_B instead of just one electron.

Application of One-Body Model to Alkyl Radicals

Under the assumption that $S^{AB} = 0$

$$E^B = E - E^A = \frac{(\Phi_B \,|\, h_{eff}^B \,|\, \Phi_B)}{(\Phi_B \,|\, \Phi_B)} \tag{18}$$

where $h_{eff}^B = \tilde{h}^B$.

$-E^B$ represents the ionization potential (I.P) of the lone electron in Φ_B which in our case is the ionization potential of the single electron in the π orbital of the alkyl radical. The derivation is completely rigorous for the alkyl radicals since $S^{AB} = 0$ for these radicals.

Since Φ_B has been already been assumed to be normalized:

$$\text{I.P.} = -E_B = \int \Phi_B(1) \, h^B_{eff}(1) \, \Phi_B(1) d\tau_1 \qquad (19)$$

This is <u>identical</u> to the expression used in II for the calculation of ionization potentials of alkyl radicals where we used only the wave function of the π electron and an h effective for the π electron.

For substituted alkyl radicals one merely changes the h^B_{eff}. To describe the effects of alkyl substituents, we assumed that one could make a perturbation on h_{eff} for the parent methyl radical

$$
\begin{array}{ccc}
h_{eff} & = & h_{eff} & + & h'_{eff} \\
(YCH_2) & & (CH_3) & & (H{\to}Y)
\end{array}
\qquad (20)
$$

and use first order perturbation theory to evaluate the elements of h'_{eff}.

Our main purpose in II was to develop a method for describing the effects of substituent groups on the ionization potentials of substituted alkyl radicals and the corresponding amines which emphasized what must be at least a close formal similarity between the two since identical substituent groups produce almost identical perturbations on the ionization potentials.

Application of Two-Body Model to Amines

Even if Φ_A and Φ_B are not rigorously orthogonal it was shown[2] that the final expression for the energy is very similar in form

$$E - E^A = \frac{(\Phi_B \mid h^B_{eff} \mid \Phi_B)}{(\Phi_B \mid f^B \mid \Phi_B)} \qquad (21)$$

where now $h^B_{eff} = \widetilde{h}^B + E^A \rho^A_1$

$$f^B = 1 - \rho^A_1$$

with $\rho^A_1(1)$ the density operator with kernel $\rho^A_1(1;2)$.

From the expression

$$E = E^A + \frac{\widetilde{E}^B - S^{AB} E^A}{1 + S^{AB}} \qquad (22)$$

it can be seen that the closer $S^{AB} \to 0$, the closer will (22) approach (19).

For substituted amines we are changing h^B_{eff} by the **same** perturbation as we are changing h_{eff} for alkyl radical

$$\begin{array}{cccc} h_{eff} & = & h_{eff} & + & h'_{eff} \\ (YCH_2) & & (CH_3) & & (H \to Y) \end{array} \qquad (20)$$

$$\begin{array}{cccc} h_{eff} & = & h_{eff} & + & h'_{eff} \\ (YCH_2) & & (NH_3) & & (H \to Y) \end{array} \qquad (23)$$

In each case we are evaluating only the elements of the same h'_{eff} with respect to the alkyl radical or amine wave functions respectively (to calculate the ionization potential itself of an amine E^B would be evaluated for only one of the electrons in the nitrogen lone pair.) The basic assumption was made in part II that one could use a wave function for the π electron of the methyl radical

$$\chi^\bullet_{\pi} \underset{(CH_3)}{} = |\phi_1(1)\ \phi_1(0)| \tag{24}$$

and the analogous expression

$$\chi^\bullet_{"\pi"} \underset{(NH_3)}{} = M\ |\psi_1(1)\ \psi_1(1')| \tag{25}$$

for the lone pair electrons in amines. "π-like" implied only that the "π-like" system is orthogonal to the other bonds in the molecule.

The perturbation calculation was outlined in part II treating integrals over the one electron $\chi^\bullet_{\pi}$ functions and over the two (CH_3) electron $\chi^\bullet_{"\pi"}$ functions in exactly the same formalistic manner for (NH_3) identical perturbing groups. Intuitively this approach had to be fruitful because from experiments we know that the same perturbing group produced the same change in ionization potential (δ_k value) regardless of the core on which it was placed.

Now, by examination of the derivation of the one-body model
for an electron outside a "core" and our extension to the two-body
model for a pair of electrons outside a "core", it can be seen that
nowhere is it invoked that Φ_B be a one electron function. It is
just as valid to have

$$\Psi'(1,2,\ldots N) = M' \mathscr{A} \left\{ \Phi_A(1,\ldots\lfloor N-2\rfloor), \ \Phi_B(\lfloor N-1\rfloor,N) \right\}$$

which is simply a general description of a system with two
distinguishable parts. Φ_B is analogous to $X^\bullet$ whether it be $X^\bullet_\pi$
$$(CH_3)$$
a one electron function, or $X^\bullet_{"\pi"}$, a two electron function.
$$(NH_3)$$
Integrals over the X's can be treated in exactly the same way. The
only thing that is important is that the h^B_{eff} be defined correctly
to include all the interaction terms of the second electron. For
our calculations of the δ_k values of the amines all of the electron
interaction terms will approximately cancel since we are looking
only at differences. The most vital point is the justification
for our having treated integrals over the two electron functions
in the same manner as those over the one electron functions.

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